


FORM PTO-1390 (2/EV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				1752-0147P	
				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/937598	
INTERNATIONAL APPLICATION NO.		INTERNATIONAL FILING DATE		PRIORITY DATE CLAIMED	
PCT/JP00/01955		March 29, 2000		March 30, 1999	
TITLE OF INVENTION SILICONE RESINS AND PHOTSENSITIVE RESIN COMPOSITIONS CONTAINING THE SAME					
APPLICANT(S) FOR DO/EO/US FUJIYAMA, Takeshi; TERAMOTO, Takeru					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. WO 00/59987</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input checked="" type="checkbox"/> is transmitted herewith.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4)</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (Original)</p> <p>10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11. to 20. below concern document(s) or information included:</p> <p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 document(s).</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information:</p> <p>1.) Zero (0) sheets of Formal Drawings</p> <p>2.) International Preliminary Examination Report (PCT/IPEA/409)</p> <p>3.) Verification of Translation</p>					

U.S. APPLICATION NO. (if known, see 37 CFR 1.20) <div style="font-size: 24pt; font-weight: bold;">09/037598</div>		INTERNATIONAL APPLICATION NO. PCT/JP00/01955		ATTORNEY'S DOCKET NUMBER 1752-0147P	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO. \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY <div style="display: flex; justify-content: space-between;"> \$ 860.00 </div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				<div style="display: flex; justify-content: space-between;"> \$ 0 </div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	9 - 20 =	0	X \$18.00	\$	0
Independent Claims	1 - 3 =	0	X \$80.00	\$	0
MULTIPLE DEPENDENT CLAIM(S) (if applicable) Yes				+	\$270.00
TOTAL OF ABOVE CALCULATIONS =				\$	1130.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0
SUBTOTAL =				\$	1130.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0
TOTAL NATIONAL FEE =				\$	1130.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	40.00
TOTAL FEES ENCLOSED =				\$	1170.00
				Amount to be:	\$
				refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1170.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account. No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-2448</u> . NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. Send all correspondence to: Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292 P.O. Box 747 Falls Church, VA 22040-0747 (703)205-8000 Date: <u>September 28, 2001</u>					
				By  Gerald M. Murphy, Jr., #28,977	

rf

PATENT
1752-0147P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: FUJIYAMA, Takeshi et al Conf.:
Int'l. Appl. No.: PCT/JP00/01955
Appl. No.: NEW Group:
Filed: September 28, 2001 Examiner:
For: SILICONE RESINS AND PHOTSENSITIVE
RESIN COMPOSITIONS CONTAINING THE
SAME

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

September 28, 2001

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

IN THE SPECIFICATION:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/01955 which has an International filing date of March 29, 2000, which designated the United States of America.--

REMARKS

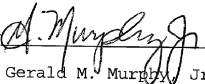
The specification has been amended to provide a cross-reference to the previously filed International Application.

Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 
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1752-0147P

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S P E C I F I C A T I O N

Title of the Invention

Silicone Resins and Photosensitive Resin Compositions Containing The Same

Field of Technology

This invention relates to silicone resins and photosensitive resin compositions containing the same useful as resist materials.

Background Technology

In the fields of a variety of electronic devices including semiconductor devices that require microfabrication, there is a rising demand for higher density and higher degree of integration of devices and finer patterning has become essential to meet this demand. Moreover, in plasma display panels (PDP), barriers of a high aspect ratio, that is, a high ratio of height to width, are in demand in order to have light of high luminance emitted by enlarging the electric discharge space for display.

A method for obtaining higher resolution in patterning is to use light of shorter wavelength in patterning of photoresists. However, the use of shorter wavelength poses a problem of the depth of focus (DOF) becoming reduced with a drop in sensitivity and aspect ratio. Multi-level resist processes have been proposed to solve this problem. According to a process of this kind, a material such as novolac and polyimide that can be readily dry-etched by oxygen plasma is deposited by spin coating on a substrate and planarized, a resist resistant to dry etching by oxygen is applied to the

surface of the planarized layer, a pattern is formed, and then the pattern is transferred to the bottom layer by anisotropic etching by oxygen plasma. As this process yields patterns of a high aspect ratio, developmental works are being conducted extensively on resist materials resistant to oxygen plasma etching.

Resist materials utilizing silicone resins are known to be highly resistant to oxygen plasma etching and, for example, compositions consisting of ladder type polysiloxane esters or polysiloxanes substituted with epoxy-containing alkyl groups and a photosensitive compound capable of generating acid upon exposure to light are proposed in JP 7-56354 (1995)A1 and JP 8-193167 (1996)A1. Moreover, resist compositions containing photosensitive silicone resins that are polysiloxanes to which a diazonaphthoquinonesulfonyloxy group and an azido group are linked are proposed in JP 6-27671 (1994)A1 and JP 6-95385 (1994)A1.

As for the barrier (rib) of a plasma display panel (PDP), a process for constructing a rib with the use of a paste formulated from photosensitive resins and inorganic powders to raise the aspect ratio is described in JP 10-62981 (1998)A1. The photosensitive resins in question are acrylic polymers and the like.

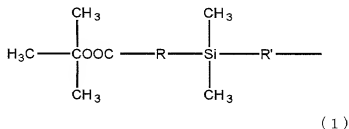
Polyorganosilsesquioxanes are occasionally abbreviated to polysiloxanes and they are known to occur in three types, that is, cage, ladder, and random. Their structures and methods of preparation are described in detail in the specifications of WO98/41566, JP 50-139900 (1975)A1, JP 6-329687 (1994)A1, JP 6-248082 (1994)A1 and elsewhere. A method for introducing functional groups to the ends of these polyorganosilsesquioxanes is also

described in detail in the aforementioned WO98/41566.

An object of this invention is to provide photosensitive silicone resins which exhibit excellent performance as resist materials for multi-level resist processes and for forming PDP barriers. Another object of this invention is to provide resist materials which exhibit excellent plasma resistance (resistance to O₂-RIE) and form patterns of a high aspect ratio.

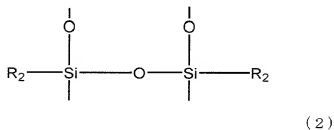
Disclosure of the Invention

This invention relates to silicone resins composed of polyorganosilsesquioxanes whose ends are partly or wholly linked to a triorganosilyl group represented by the following general formula (1)



(wherein R is a divalent organic group and R' is a divalent group or a direct bond).

This invention also relates to the aforementioned silicone resins wherein the polyorganosilsesquioxanes have a repeating unit represented by the following general formula (2)



(wherein R₂ is an unsubstituted or substituted phenyl group) and the

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average number of repeating units is 2-5,000.

Furthermore, this invention relates to the aforementioned silicone resins wherein the polyorganosilsesquioxanes consist of one type or a mixture of two types or more selected from ladder type, cage type, and mixed cage-ladder type and the weight average molecular weight Mw is 800-100,000 as determined by gel permeation chromatography (GPC) and calibrated against polystyrene.

Still more, this invention relates to the aforementioned silicone resins wherein R is $\cdot R_1COOX_1\cdot$ or $\cdot R_1COOX_1Si(CH_3)_2O\cdot$ (wherein R_1 is the divalent residue of a polycarboxylic acid or derivative thereof and X_1 is a divalent group).

Still further, this invention relates to photosensitive resin compositions formulated from the aforementioned silicone resins and a photogenerator of acid.

Finally, this invention relates to a process for preparing the aforementioned silicone resins which comprises treating polyorganosilsesquioxanes with $X-Si(R_3)_2Y$ or $X-Si(R_3)_2OSi(R_3)_2Y$ [wherein X and Y are groups capable of linking with carboxyl groups or functional groups capable of reacting with terminal OH groups or terminal OM groups (M is an alkali metal) of the backbone of polyorganosilsesquioxanes and R_3 is a monovalent organic group] to give modified polyorganosilsesquioxanes containing X or Y at all or a part of their terminal positions, and treating the terminal groups with $t-BuOOC\cdot R_1\cdot COOH$ (wherein t-Bu is t-butyl group and R_1 is the divalent residue of a polycarboxylic acid or derivative thereof). The group R_3 here is a monovalent organic group such as alkyl and aryl,

preferably methyl, and R_3 in a given molecule may be of the same kind or of two or more kinds.

Photosensitive silicone resins of this invention are structurally polyorganosilsesquioxanes to which a triorganosilyl group represented by the aforementioned general formula (1) is linked to all or a part of the ends of the backbone chain. The backbone chain may be represented by the general formula $(R_2Si_2O_3)_n$ and n designates the number of repetition and is 2 or more. Preferable polyorganosilsesquioxanes have a repeating unit represented by the aforementioned general formula (2) and the average number of repeating units is 2-5,000, more preferably 5-500. The group R_2 is a monovalent organic group and may be a hydrocarbon group such as aryl and alkyl and an alkoxy group, but R_2 is preferably an alkyl group with 1-6 carbon atoms or an unsubstituted or substituted phenyl group, more preferably a phenyl group.

In the triorganosilyl group represented by the general formula (1), R is a divalent organic group and, as indicated by the aforementioned general formula (1), R may be said to contain the residue of a carboxylic acid. The group R' designates a divalent group or a direct bond and, in the case of a divalent group, it is linked on the other side to the terminal $Si-O\cdot$ group of polyorganosilsesquioxanes. The *t*-butyl group at the end of of the triorganosilyl group comes off to leave a free carboxyl group behind when it contacts the acid generated from a photogenerator of acid thereby enhancing the the alkali solubility of silicone resins and it is this property that is utilized in patterning.

Carboxylic acids which give the divalent group R include monocarboxylic

acids such as benzoic acid and acetic acid and polycarboxylic acids and they are preferably polycarboxylic acids. Such polycarboxylic acids include pyromellitic acid, trimellitic acid, phthalic acid, biphenyldicarboxylic acid, biphenyltetracarboxylic acid, biphenylhexacarboxylic acid, benzophenonedicarboxylic acid, benzophenonetetracarboxylic acid, diphenyl ether dicarboxylic acid, diphenyl ether tetracarboxylic acid, diphenyl sulfone dicarboxylic acid, diphenyl sulfone tetracarboxylic acid, diphenyl sulfide dicarboxylic acid, diphenyl sulfide tetracarboxylic acid, benzanilidedicarboxylic acid, benzanilidetetracarboxylic acid, benzanilidepentacarboxylic acid, cyclohexanedicarboxylic acid, cyclohexenedicarboxylic acid, succinic acid, adipic acid, maleic acid, and fumaric acid.

In the case of polycarboxylic acids, the carboxyl group not linked to *t*-butyl group may be present as free carboxyl (-COOH) or in the form of ester or salt. In particular, it is preferable that one of the carboxyl groups forms an ester linkage with Si either directly or through a divalent group X as illustrated by $\text{t-Bu-OOC-R}_1\text{-COO-X-Si(Me)}_2$. Here, the group R in the general formula (1) corresponds to $\text{R}_1\text{-COOX}$ and X is a divalent group such as alkylene or arylene or a direct bond.

In case polycarboxylic acids is tricarboxylic or higher acids, at least one of the carboxyl groups remains intact and it may remain so or it may be converted to the neutral form such as ester and salt. Alkali solubility becomes poorer if the carboxyl group in question exists in the neutral form such as ester. The acid from a photogenerator of acid contributes to enhance alkali solubility by dissociating the *t*-butyl group and generating a

carboxylic acid. In the cases in which patterning is effected by utilizing this phenomenon, there should desirably be a large difference in alkali solubility between the exposed and unexposed regions and, for this reason, the free carboxyl groups are converted to esters, preferably to t-butyl esters by treating with t-butyl alcohol or derivative thereof.

The group R may contain not only the residue of a carboxylic acid but also a part of the residue of a terminal modifier which modifies the ends of polyorganosilsesquioxanes as described above. A suitable terminal modifier can be represented by $X-Si(CH_3)_2-Y$ in which Y is a functional group capable of linking to the backbone polyorganosilsesquioxanes and X is a functional group capable of linking to a group such as carboxyl. For example, a terminal modifier represented by $X-Si(CH_3)_2-O-Si(CH_3)_2-Y$ [wherein Y is a functional group such as epoxy capable of reacting with the terminal OH or OM group (M is an alkali metal)] reacts with polyorganosilsesquioxanes at one end through Y to give polyorganosilsesquioxanes containing X at the other end. The X-terminated polyorganosilsesquioxanes then react with the aforementioned polycarboxylic acid or derivative thereof to give a product whose R contains $-CH_2-CH(OH)-$ in case X is an epoxy group. A variety of groups such as ester and amide can be formed by changing X. In the aforementioned terminal modifier, X and Y may naturally be identical with or different from each other, but one of them needs to be reactive with the terminal group (or terminal group being generated during the reaction) of polyorganosilsesquioxanes and the other needs to be reactive with a group such as carboxyl or derivative thereof. As is apparent from the above description, the backbone polyorganosilsesquioxanes and the triorganosilyl

group represented by the general formula (1) are linked not necessarily through a siloxane linkage but through an appropriate group.

Photosensitive silicone resins of this invention can be prepared by utilizing a known reaction. In the case of polyorganosilsesquioxanes containing terminal silanol, for example, the terminal modification is effected by treating the polymers with a monohalide such as $X-Si(CH_3)_2-Cl$. One of preferable procedures for terminal modification is to treat polyorganosilsesquioxanes such as silanol-free cage type and/or ladder type octaphenylsesquioxane with a terminal modifier such as the aforementioned $X-Si(R_3)_2-O-Si(R_3)_2-X$ in the presence of an alkali metal catalyst to give X-terminated polyorganosilsesquioxanes.

A silicon atom in polyorganosilsesquioxanes and the silicon atom in a terminal modifier such as $X-Si(CH_3)_2-Y$ tend to undergo exchange reaction and a procedure utilizing this property is also effective for terminal modification. In this case, at least one of X and Y needs to be reactive with a carboxyl group. Moreover, it is possible to effect the aforementioned reaction and the exchange reaction simultaneously by using Y as a group capable of reacting with the end of polyorganosilsesquioxanes.

A preferable procedure for preparing silicone resins of this invention from terminally modified polyorganosilsesquioxanes is, for example, to treat the terminally modified polyorganosilsesquioxanes with an acidic ester prepared by the reaction of t-butyl alcohol with a polycarboxylic acid or derivative thereof such as acid anhydride in the presence of a quaternary ammonium salt as a catalyst.

Silicone resins of this invention have a weight average molecular weight

of 800-100,000, preferably 5,000-50,000, as determined by GPC and calibrated against polystyrene. The silicone resins in question are solid at normal temperature and soluble in many organic solvents such as esters and ethers. Furthermore, silicone resins of this invention are preferably polyorganosiloxanes represented by the general formula $(C_6H_5Si_{3/2})_n$ having a triorganosilyl group represented by the general formula (1) at all or 10% or more of their replaceable ends, for example, one triorganosilyl group for $n = 4-20$, preferably one for $n = 2-8$.

Silicone resins of this invention are best suited for use as positive resist materials. In such end uses, it is possible to incorporate generators of acid or a variety of additives in order to enhance sensitivity or improve heat or plasma resistance.

Additives indispensable to photosensitive resin compositions of this invention are photogenerators of acid. Such photogenerators of acid include, but are not limited to, sulfonium salts such as triphenylsulfonium trifluorosulfonate, triphenylsulfonium trifluoromethaneantimonate, triphenylsulfonium benzenesulfonate, and cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethanesulfonate, iodonium compounds such as diphenyliodonium trifluoromethanesulfonate, and N-hydroxysuccinimide trifluoromethanesulfonate. A detailed description of the chemical formulas and actions of these photogenerators of acid is found in the aforementioned JP 8-193167 (1996)A1 and "New Development of Practical Polymer Resist Materials", p. 57 (in Japanese) published by CMC. A photogenerator of acid is normally added at a rate of 0.2-25% by weight of total solids.

An organic solvent is used to adjust the viscosity. Preferable solvents include, but are not limited to, Methyl Cellosolve acetate, propylene glycol monoethyl ether acetate, methyl lactate, ethoxyethyl acetate, methyl pyruvate, methyl methoxypropionate, N-methylpyrrolidinone, cyclohexanone, methyl ethyl ketone, dioxane, ethylene glycol monomethyl ether acetate, and diethylene glycol monoethyl ether.

Photosensitive resin compositions of this invention contain the aforementioned photosensitive silicone resins and photogenerators of acid as indispensable components and often contain solvents. In addition, it is permissible to incorporate surfactants, colorants, stabilizers, coating improvers, and inorganic powders as needed.

Photosensitive silicone resins of this invention and their compositions can be used as resist materials and barrier materials of PDP. Although there is no restriction on the mode of their use as resist material, they are best suited for multi-level resist processes.

According to a multi-level resist process, a material such as novolac which can be readily dry-etched by oxygen plasma is applied by spin coating to the surface of a substrate, a material of this invention is applied thereto, the layers are exposed to a laser such as excimer to generate acid from a photogenerator of acid and let the acid dissociate silicone resins, patterning is effected by developing with an aqueous alkaline solution, and the bottom layer resist is etched by oxygen plasma to give a pattern of a high aspect ratio.

As for the preparation of barrier materials of PDP, methods such as sandblasting, embedding, and photopaste are known. Since any of the

methods uses photosensitive resist materials, materials of this invention can be used as such. In particular, when applied to the photopaste method or the like in which the resist remains unrecovered, materials of this invention can fully produce the effect of excellent plasma resistance.

Preferred Embodiments of the Invention

Example 1

Phenylsilsesquioxane containing glycidyl group was synthesized with reference to Reference Example 1 and Example 3 described in PCT/JP98/01098 (WO98/41566) and JP 10-251407 (1998)A1.

Synthetic Example 1

[Synthesis of cage type octaphenylsilsesquioxane]

In 500 cc of toluene was dissolved 105 g (0.5 mole) of phenyltrichlorosilane and the mixture was shaken with water until the hydrolysis was completed. The hydrolysis product was washed with water, mixed with 16.6 cc (0.03 mole) of commercially available 30% methanol solution of benzyltrimethylammonium hydroxide, and the mixture was heated at reflux temperature for 4 hr.

Thereafter, the whole mixture was cooled and left standing for approximately 96 hr. After this time elapsed, the resulting slurry was again heated at reflux temperature for 24 hr, cooled, and filtered to give about 75 g of cage type octaphenylsilsesquioxane ($C_6H_5SiO_{3/2}$)₈. In infrared spectrometry of the product, absorption bands assignable to Si-C₆H₅ were observed at 1595 cm⁻¹ and 1430 cm⁻¹ and an absorption band assignable to

the antisymmetric stretching vibration of Si-O-Si was observed at 1135 cm^{-1} while an absorption band assignable to Si-OH was not observed at 3400 cm^{-1} . In ^{29}Si -MASNMR determination, only one sharp signal of Si nucleus in the cage type octaphenylsilsesquioxane was observed at -77 ppm . The number average molecular weight Mn was 760 when determined by GPC with o-dichlorobenzene used as a flowing solvent and calibrated against polystyrene.

Synthetic Example 2

[Synthesis of phenylsilsesquioxane oligomer containing glycidyl group]

To a reaction vessel were added 100 g of the cage type octaphenylsilsesquioxane, 70.3 g of 1,3-bis(3-glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane, 400 g of toluene, and 4 g of tetramethylammonium hydroxide pentahydrate and the mixture was heated at reflux temperature with vigorous stirring for 7 hr. The reaction mixture was a white suspension at the start because white powders of the cage type octaphenylsilsesquioxane did not dissolve in toluene, but the powders gradually dissolved as the reaction progressed and nearly all of them dissolved after 7 hr to give a colorless transparent solution. The solution was cooled to room temperature, a precipitate of the unreacted tetramethylammonium hydroxide was removed by filtration, and the filtrate was poured into 2,000 g of excess methanol to reprecipitate phenylsilsesquioxane containing a terminal glycidoxy group. The viscous precipitate was washed with methanol and distilled to strip off the methanol and the residual toluene to give 120 g of glycidyl-containing

phenylsilsesquioxane oligomer as a pale yellow transparent viscous product. The epoxy equivalent as determined by the hydrochloric acid-pyridine method was 945 g/eq. The number average molecular weight Mn determined by GPC and calibrated against polystyrene was 20,000.

Synthetic Example 3

[Synthesis of carboxylic acid containing t-butyl ester group]

To a 1-l three-necked flask were added 62 g of maleic anhydride, 74 g of sodium t-butoxide, and 400 g of propylene glycol monomethyl ether acetate, 0.44 g of sodium methoxide was added as a catalyst, and the mixture was heated under reflux at 150°C for 2 hr. The mixture was allowed to cool to room temperature and 0.85 g of concentrated hydrochloric acid was added. The resulting brown reaction mixture was placed in an eggplant-shaped flask and the solvent propylene glycol monomethyl ether acetate was distilled off in an evaporator. Thereafter, the remainder was dissolved in 600 g of dichloromethane and washed with 500 g of distilled water three times. The dichloromethane was evaporated off to give a carboxylic acid containing a t-butyl ester group as a brown viscous liquid in 90% yield.

Synthetic Example 4

[Synthesis of phenylsilsesquioxane containing t-butyl ester group]

To a three-necked flask were added 100 g of the glycidyl-containing phenylsilsesquioxane oligomer prepared in Synthetic Example 2, 14 g of the carboxylic acid containing a t-butyl ester group prepared in Synthetic Example 3, 100 g of propylene glycol monomethyl ether acetate as a solvent,

and 0.2 g of tetraethylammonium bromide as a catalyst and the mixture was heated at 90 °C with stirring for 2 hr to give phenylsilsesquioxane containing a t-butyl ester group as a brown viscous liquid in 80% yield.

Example 2

(1) Experiments on patterning using resins of this invention

A photosensitive resin solution was prepared by dissolving 1 g of triphenylsulfonium triflate ($\text{Ph}_3\text{S}^+ \text{OTf}^-$) or a photogenerator of acid in 100 g of a solution of the phenylsilsesquioxane containing t-butyl ester group prepared in Example 1 in propylene glycol monomethyl ether acetate and the solution was applied by spin coating to a glass substrate and dried at 70°C for 15 minutes to form a $0.3 \mu\text{m}$ -thick film. The film was irradiated with UV (248 nm) through a mask and developed by a 3% aqueous solution of tetramethylammonium hydroxide to give a clear pattern (line and space $0.3 \mu\text{m}$). It was confirmed that the resin exhibits a property of positive resist.

(2) Experiments on two-level resist patterning using resins of this invention

A silicon wafer was spin-coated with a $1 \mu\text{m}$ -thick bottom resist layer of cresol novolac and a $0.1 \mu\text{m}$ -thick top positive resist layer of the phenylsilsesquioxane containing t-butyl ester group prepared in Example 1, exposed to far UV (193 nm) excimer laser, and developed with a 2% aqueous solution of tetramethylammonium hydroxide to form a clear pattern in the top layer (line and space $0.1 \mu\text{m}$). Thereafter, the bottom resist was etched by O_2 -RIE and the top resist was removed by CF_4 -RIE to form clearly

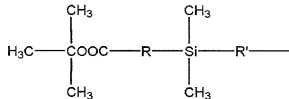
patterned cresol novolac with a linewidth of $0.1\ \mu\text{m}$ and an aspect ratio of 10.

Industrial Applicability

Silicone resins of this invention and their compositions give resists of excellent plasma resistance and make precision patterning of electronic devices feasible. They are also well suited for barrier materials of PDP and, moreover, exhibit excellent performance as resist materials for multi-level resist processes and for forming barriers of PDP. In addition, they exhibit excellent plasma resistance (resistance to O_2 -RIE) and, when used in patterning, give patterns of a high aspect ratio.

What is claimed is:

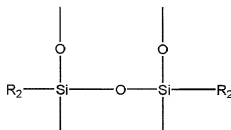
(1) Silicone resins wherein a triorganosilyl group represented by the following general formula (1)



(1)

(wherein R is a divalent organic group and R' is a divalent group or a direct bond) is linked to all or a part of the ends of the backbone chain of polyorganosilsesquioxanes.

(2) Silicone resins as described in claim 1 wherein the polyorganosilsesquioxanes contain a repeating unit represented by the following general formula (2)



(2)

(wherein R₂ is an unsubstituted or substituted phenyl group) and the average number of repeating units is 2-5,000.

(3) Silicone resins as described in claim 1 wherein the polyorganosilsesquioxanes consist of one type or a mixture of two types or more selected from ladder type, cage type, and mixed cage-ladder type and

their weight average molecular weight Mw determined by gel permeation chromatography (GPC) and calibrated against polystyrene is 800-100,000.

(4) Silicone resins as described in claim 1 wherein the group R in the general formula (1) is $\text{-R}_1\text{COOX}_1\text{-}$ or $\text{-R}_1\text{COOX}_1\text{-Si(CH}_3)_2\text{-O-}$ (wherein R_1 is the divalent residue of a polycarboxylic acid or derivative thereof).

(5) A process for preparing silicone resins as described in claim 1 which comprises treating polyorganosilsesquioxanes with $\text{X-Si(R}_3)_2\text{-Y}$ or $\text{X-Si(R}_3)_2\text{OSi(R}_3)_2\text{-Y}$ (wherein X and Y are groups capable of linking to carboxyl groups or functional groups capable of reacting with the terminal OH or OM group (M is an alkali metal) and R_3 is a monovalent organic group) to give terminally modified polyorganosilsesquioxanes in which X or Y is present at all or a part of their ends, treating the terminally modified polyorganosilsesquioxanes with an acidic ester prepared by the reaction of t-butyl alcohol with a polycarboxylic acid or derivative thereof to give silicone resins in which the triorganosilyl group represented by the general formula (1) is linked to all or a part of the ends of the backbone of polyorganosilsesquioxanes.

(6) Photosensitive resin compositions comprising the silicone resins as described in any one of claims 1 to 4 and a photogenerator of acid.

BIRCH, STEWART, KOLASCH & BIRCH, LLP

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1752-0147P

FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title:

Silicone Resins and Photosensitive Resin Compositions Containing
The Same

Fill in Appropriate
Information -
For Use Without
Specification
Attached:

the specification of which is attached hereto. If not attached hereto,

the specification was filed on _____ as

United States Application Number _____; and /or

the specification was filed on March 29, 2000 as PCT

International Application Number PCT/JP00/01955; and was

amended under PCT Article 19 on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Insert Priority
Information:
(if appropriate)

Prior Foreign Application(s)

89441/1999

(Number)

Japan

(Country)

03/30/1999

(Month/Day/Year Filed)

Priority Claimed

☒

Yes

☐

No

(Number)

(Country)

(Month/Day/Year Filed)

☐

Yes

☐

No

(Number)

(Country)

(Month/Day/Year Filed)

☐

Yes

☐

No

(Number)

(Country)

(Month/Day/Year Filed)

☐

Yes

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No

(Number)

(Country)

(Month/Day/Year Filed)

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Yes

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No

Insert Provisional
Application(s):
(if any)

I hereby claim the benefit under Title 35, United States Code, §119(c) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More Than 12 Months (6 Months for Designs) Prior To The Filing Date of This Application:

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Application No.

Date of Filing (Month/Day/Year)

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(if appropriate)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Insert Prior U.S.
Application(s):
(if any)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor:
Insert Name of Inventor
Insert Date This
Document is Signed

Insert Residence
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Insert Post Office
Address

Full Name of Second
Inventor, if any

see above

Full Name of Third
Inventor, if any

see above

Full Name of Fourth
Inventor, if any

see above

Full Name of Fifth
Inventor, if any

see above

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Residence (City, State & Country)		CITIZENSHIP	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			

* DATE OF SIGNATURE